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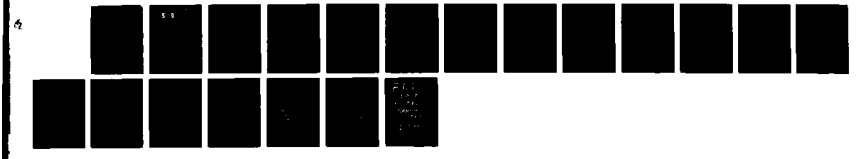

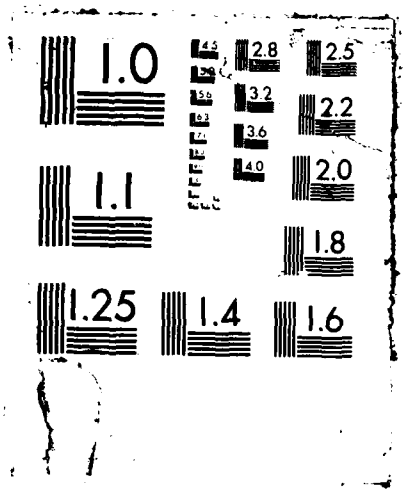
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CONTRASTING CONDUCTANCE/VISCOSITY RELATIONS IN LIQUID STATES OF VITREOUS AND POLYMER "SOLID" ELECTROLYTES

by

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ABSTRACT

In order to contrast conductivity mechanisms in fast ion glassy and rubbery polymer electrolytes, the *liquid* states of two prototypical cases have been studied. Viscosity and conductivity measurements have been performed on molten (as opposed to glassy) $(AgCl)_{0.35}$ $(Ag(I))_{0.45}$ $(CsCl)_{0.20}$ and on solutions of sodium triflate in low molecular weight PPG (as opposed to high mw, 10^6 rubbery solid PPG - called PPO). Both types of system show non-Arrhenius viscosity with divergent behavior near T_g. The energetics of the conductivity processes, however, are very different. This is emphasized by reduced temperature scale (T/T_g) plotting of (temperature-dependent) activation energies. For the polymer salt systems, as for normal molten salt systems and aqueous solutions, conductance and viscosity energetics are comparable - the processes are coupled. Reduced temperature plots of polymer solutions and glassforming aqueous solution data show the relative importance of T_g and ion association factors in limiting polymer electrolyte performance.

INTRODUCTION

Amorphous solid conductors offer the best practical solutions to the ambient temperature solid state electrochemical device electrolyte problem because of their combination of high ionic conductivity and ease of fabrication into thin films. Within the amorphous solid family there are two contrasting subgroups, the vitreous conductors and the elastomeric polymer + salt conductors. It is generally recognized that the mechanism of conductance in these subgroups is different[1,2]. In the polymer electrolyte case good performance depends on the service temperature being far above the glass-rubber transition temperature T_g, whereas, for vitreous electrolytes, the requirements of dimensional stability and stability against devitrification, demand the reverse service temperature/T_g relationship. This implies that the mobile ion - vitreous matrix interactions must be weak in superionic glasses, whereas it would appear that the

reverse must be true in polymer electrolytes in view of the solvation interaction on which the solubility of salt in polymer depends.

While these distinctions seem entirely reasonable, there is a lack of quantitative physical data on which to base them. We thought some comparative study of the two types of systems in common regions *above* T_g could make a useful contribution to understanding the respective mechanisms. So far there has only been one study of conductivity in the *liquid* state of a superionic conducting glass system - the recent work of Kawamura and Shimoji on AgI - Ag_2MoO_4 mixtures[3]. However, the comparison we wish to make is between viscosity and conductance in the two types of system, and no viscosity data are available for the liquid state of AgI - Ag_2MoO_4. Since most of the superionic conducting systems studied to date contain oxyanions and therefore are rather high-melting and also corrosive in the liquid state there has been some reluctance to develop the techniques necessary to measure their liquid state properties.

The resolution of this problem is found in the all-halide superionic glass systems recently described in papers from this and other laboratories[4–6]. The liquid states of these low melting materials can be studied by conventional molten salt techniques[7] using pyrex glass capillary cells of high cell constant to measure the (very low) liquid resistivities, and Ubbelohde capillary viscometers to determine the (very low) viscosities.

We have carried out a series of measurements on two compositions in the system AgI - AgCl - CsCl, one of which has a very high ambient temperature conductivity, and also a subambient T_g, −11.5°C, which is not far above that of T_g in the much studied rubbery polymer electrolyte system $(PPO)_9\ NaCF_3SO_3$.[7] (T_g =).

The high molecular weight polymer (mw ≡ 10^6) is rubbery rather than liquid because of the large molecular weight dependence of the viscosity in polymer electrolytes, and the chain entanglement phenomenon.[8] Since we wish to compare the energetics of viscous flow and electrical migration processes and since the molecular weight dependence of viscosity in pure PPG polymers appears to reside mainly in the pre-exponent of the appropriate expression for the viscosity,[8] our objectives can be met by investigating solutions in low molecular weight solvents. Thus, to compare with the liquid Ag^+ superionic conductor system, we choose solutions of $NaCF_3SO_3$ in PPG solvents of molecular weights differing by one order of magnitude viz. 425 and 4000, keeping the monomer/salt ratio (O/Na) constant at 16:1.

EXPERIMENTAL

The AgI-AgCl-CsCl melts were prepared by weighing of analytical grade reagents from Merck and Mallinkrodt which were used without further purification. The weighed mixtures were fused and filtered into a 1.5cm diameter test tube which was just wide enough to accept a standard pyrex capillary conductivity cell, of cell constant 574.8 (determined with 0.1m KCl). The test tube with contents was mounted in Al block furnace, the temperature of which was controlled to ± 0.1°C by means of a Eurotherm proportional temperature controller. The temperature was uniform to 0.1°C over the length of the capillary cell. Measurements of the conductance and capacitance were made using an automated Hewlett-Packard model 4192A admittance bridge, and the dc conductivity was determined from a complex admittance plot. For the same liquid, the kinetic viscosity was determined using a small-sample Ubbelohde viscometers, of viscometer constants .01444 and .003978 centistokes/sec. The viscometer was mounted in a tall aluminum block[9] which guaranteed that the variation of temperature across the capillary section of the viscometer was no more than 0.1°C. The same melt which had been used in the conductivity experiment was then transferred into the viscometer and readings were made at approximately 10K intervals in the temperature range from 300°C down to a low limit of ~ 190°C determined by the freezing of the supercooled liquid.

The polymer electrolytes were prepared by vacuum drying of pure 425 and 4000 MW polymers obtained from Polyscience Corp. at 65°C for five hours and then adding measured amounts of sodium trifilate dissolved in methanol. The methanol was then quantitatively removed by vacuum oven drying at 65°C. The conductivities of these solutions were much lower than those of the molten salts so a low cell constant all-metal conductivity cell was used. This had the advantage that the low temperature, low conductivity, range could be explored and the frequency-dependent characteristics of the bulk electrolyte solutions determined. Measurements were conducted in an automated system using the HP 4192 bridge in the temperature range -20 to +135°C.

Viscosities of the (higher viscosity) polymer-salt solutions were determined using a digital Brookfield rotating cylinder viscometer. The commercial Brookfield thermo cell containing the sample was controlled to ± 0.1°C by a Eurotherm on/off controller.

Glass transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer DSC-4) at 10 deg/min scans.

RESULTS

Results of the conductivity measurements on the compositions 0.6 AgCl · 0.4CsCl and 0.35AgCl · 0.45AgI · 0.20CsCl are displayed as specific resistivities in Fig. 1 in the form of an Arrhenius plot. The corresponding viscosity data are included in Fig. 1, using a log scale of the same division size, so that the plot slopes are proportional to the respective activation energies. The higher temperature dependence of the viscosity in each case is obvious.

In Fig. 2 the conductivity data for the R = 16 sodium triflate solutions in 425 and 4000 MW PPG are displayed. The data in this case cover some five orders of magnitude in σ. The values plotted are obtained in each case from the complex impedance plots, examples of which are shown as an insert to Fig. 2. In Fig. 3 the viscosity data determined over a smaller temperature range for the same two solutions are shown. The difference in viscosity between t e two solutions is in part due to the molecular weight dependence of the viscosity v hich is general for polymers and in part to a molecular weight dependence of the g ass transition temperature for equal concentration electrolyte solutions which is not ound for the pure polymers. The glass transition temperatures were determined by differential scanning calorimetry using a Perkin Elmer DSC4 instrument and the 10 deg/min scans are shown in the insert to Fig. 3.

DISCUSSION

In recent articles one of us has discussed the phenomenon of fast ion conduction in glasses in terms of the decoupling of electrical modes from viscoelastic modes during cooling from the high temperature liquid state.[2] In the absence of suitable data on liquid fast ion conductors, these speculations have taken their experimental support from the literature on liquid states of the classic alkali oxide glasses[10]. The decoupling is demonstrated by converting the viscosity and conductivity data into appropriate relaxation times for shear and electrical stresses and then comparing the effect of temperature on the system in terms of the relative behavior of these relaxation times. Average relaxation times may be obtained from the viscosity and conductivity data using Maxwell relations which connect the liquid-like properties shear viscosity η_s and d.c. resistivity ρ to the solid-like properties shear modulus G_∞ and electrical modulus M_∞. The relations are

$$\tau_s = \eta_s/G_\infty \qquad (1)$$

$$\tau_\sigma = \rho e_0 / M_\infty \qquad (2)$$

where e_0 is the primitivity of free space.

The electrical modulus can be obtained, to good approximation, from the *glassy* state measurements of Liu et. al.[4] on the superionic glass states of the AgI-AgCl-CsCl system. There are, unfortunately, no frequency-dependent viscosity/shear modulus data for this system, but a reasonable value for G_∞ may be taken from the results of a light scattering study[11] of the glassforming salt system $2Ca(NO_3)_2 \cdot 3KNO_3$, which has a glass transition temperature 68°C not too different from that of the more viscous composition of the present study, 20°C. (G_∞ usually scales with T_g, so the error involved is probably no greater than 15%).

The conductivity and shear relaxation times for AgI-AgCl-CsCl melts are compared in Fig. 4 where they are combined with conductivity relaxation times in the glassy state obtained from the work of Liu, et. al.,[4] and with an approximate shear relaxation time at the glass transition temperature based on the known results for comparable systems.[12] By using a reduced temperature scale based on T_g as scaling parameter, we collapse the viscosity data almost to a single curve while the electrical relaxation data show two distinct plots which reflect the different extents to which the conducting modes in these two compositions become decoupled from the viscoelastic modes during cooling. Most of the decoupling evidently occurs at lower thermal excitations approaching T_g where unfortunately measurements were precluded by crystallization. A good idea of the conductivity behavior in this regime may be obtained from the unbroken σ/T plots seen in Ref. 3. We note that in the most favorable case, the conductivity relaxation time decreases by only two orders of magnitude between the high temperature liquid state regime of the present study and the onset of the glassy state, implying that the decoupling is almost complete. The decoupling can be quantified through the relaxation time ratio τ_s/τ_σ which has been called the "decoupling index" R_τ[2], and in the best case in the present system reaches 10^{13} at T_g. It is notable that even in the highly fluid state of this system explored in our measurements, the conductivity time is still almost an order of magnitude shorter than the shear relaxation time, though extrapolation to $T_g/T = 0$ implies that the pre-exponent for each process is essentially the same (and corresponds well with quasilattice vibration time found for similar systems from far infrared spectroscopic studies).[14]

The fact that the rubbery polymer electrolytes[15] can conduct electricity almost as well as the *liquid* polymer electrolytes of this study (particularly if the comparison is

made at equal T/T_g) (see below) might suggest that, in polymer electrolytes, the conducting modes are also highly decoupled from the matrix modes as in the glassy FIC case. However, the distinction between the two cases is made obvious if we plot the (temperature-dependent) activation energies for both conductivity and viscosity on the same diagram. This is done for both molten salt and polymer systems in Fig. 5, using a reduced temperature scale to remove those differences at given temperatures which are due only to the different temperature intervals above T_g. Included in Fig. are (i) data for another molten salt system in which there are no "fast" ions, viz., the tetra-substituted ammonium iodide (methoxy ethyl trimethyl ammonium iodide) prepared by Cooper as a glass-forming solvent for LiI,[16] and (ii) data for the much studied model molten salt system $2Ca(NO_3)_2 \cdot 3KNO_3$.[17-19] The important point of Fig. 5 is the manner in which both viscosity and conductivity activity energies increase rapidly to very large values as T_g is approached in all cases except the ("decoupled") conductivity of the superionic glass-former. The spread of curves is of secondary importance and reflects differences in "fragility" amongst the different systems.[21] (The "fragility" of a glassforming liquid is a description of the departure from the Arrhenius behavior as the liquid viscosity changes from a defined value at T_g (10^{13} poise by classical definition or ~ 10^{11} poise at the calorimetric T_g) to a high temperature limit of ~ 10^{-4} poise. The high temperature liquid is related to the quasi-lattice vibration frequency ν ($\eta_{lim} \equiv G_\infty/\nu$[13]). Such plots are illustrated by the insert to Fig. 5. Differences in fragility are emphasized when comparing derivative properties as in Fig. 5).

Fig. 5 suggests that when the *energetics* of transport processes are compared at equal T_g, polymer electrolytes and ordinary molten salts have much in common. The activation energies of both the conductance process and viscous flow process are in each case comparable. Thus, with respect to the fundamental mass transporting energy fluctuation, the polymer-salt conductivity is *not* decoupled from the matrix motions.

Recalling that the resistivity activation energy data designated ρ NaTr12/10^6 in Fig. 5 (for sodium triflate O Na = 12 in high molecular weight (10^6) PPO) are for a *rubbery solid* material, the conclusion to be drawn is that both high molecular weight polymer electrolytes and superionic glasses are very distinct from ordinary salts and solutions, but that the origins of their distinction are quite different. In superionic glasses it is because the basic energetics of transport are very different; the energy required for a fast-ion diffusive step to occur is small at all temperatures due to energy decoupling from structural and viscous modes with falling temperature. In rubbery

"solid" polymers on the other hand, it is because the non-ergodic component of the viscosity, the pre-exponential factor is so large that quite moderate decreases in temperature are sufficient to cause the macroscopic fluidity to vanish i.e. to impose a finite shear modulus on the system at ambient temperature. This occurs while the energetic events which control local rearrangements of chain segments, hence ion transporting motions, remain quite probable, indeed just as probable as in a molten salt of comparable T_g according to Fig. 5.

With the energetics of conductivity in polymer electrolytes are thus established as unexceptional in character, it remains to discuss the origin of their relatively poor performance as electrolytes compared with aqueous solutions.

One factor which must be of major importance is the difference in temperature at which the probability of a local ion-transporting rearrangement becomes vanishingly small, which we can associate with the glass transition, T_g. T_g is considerably higher for all polymer solutions than for all but the most concentrated aqueous solutions. The effect of T_g on electrolyte performance can be scaled out by reduced temperature plotting to reveal other factors affecting the relative performance. Thus we compare, in T_g-reduced form in Fig. 6, the conductivity performance for the polymer electrolyte solutions of this study, and of Armand's rubbery polymer electrolyte, with that of an aqueous solution, $LiCl \cdot 5H_2O$, for which data over an exceptionally wide range of temperature and conductivity exist.[22-24]

We include, in Fig. 1, data for the tetra-substituted ammonium iodide (seen in Fig. 5) and its glass-forming mixture with LiI, to show the broad view similarity of the aqueous solution and the anhydrous molten ammonium salt. These are two systems which we believe approach the condition described by the term "completely dissociated." Ionic dissociation, which is a well-defined concept for dilute solutions, requires an operational definition for systems as highly concentrated in ions as those under consideration in this paper. Noting that the relaxation times for shear and electrical stresses are essentially the same in the $LiCl \cdot 5H_2O$ system,[21] we assume that the behavior of the concentrated $LiCl + H_2O$ solution seen in Fig. 6 is that of a "fully dissociated system." The order of magnitude lower conductivity of the polymer triflate solutions is therefore to be attributed to some form of "ion association." We take this to mean that, relative to the aqueous solution, ions in the polymer solutions spend as much as 90% of their time in sufficiently intimate association with ions of the opposite charge that, when an energy fluctuation sufficient for local structure rearrangement

occurs, the oppositely charged ions move in unison - i.e. no net current flows.

The spectroscopic signatures, though not the lifetimes, of contact and solvent separated ion pairs and clusters in the present solutions have recently been reported by Torell and coworkers,[25] and lend semi-quantitative support to the latter conclusion. In particular, the increasing separation of aqueous and polymer curves at high T accords with the spectroscopic evidence for increasing association at the higher temperatures.[25,26] A study in which systematic variations in composition between aqueous and polymer solvent environments are made, is evidently needed to clarify this phenomenology.

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26.

FIGURES

Figure 1. Arrhenius plot of the specific resistivity ρ, and viscosity η, for the molten salt mixtures 0.6 AgCl · 0.4 CsCl, and 0.35 AgCl · 0.45 AgI · 0.20 CsCl. Note difference in resistivity and viscosity plot slopes.

Figure 2. Specific conductivity of sodium triflate solutions O/Na = 16, in PPG solutions with respective molecular weights 425 and 4000. Insert: complex impedance plots of the 1:16 $NaCF_3SO_3$ PPG 4000 sodium triflate

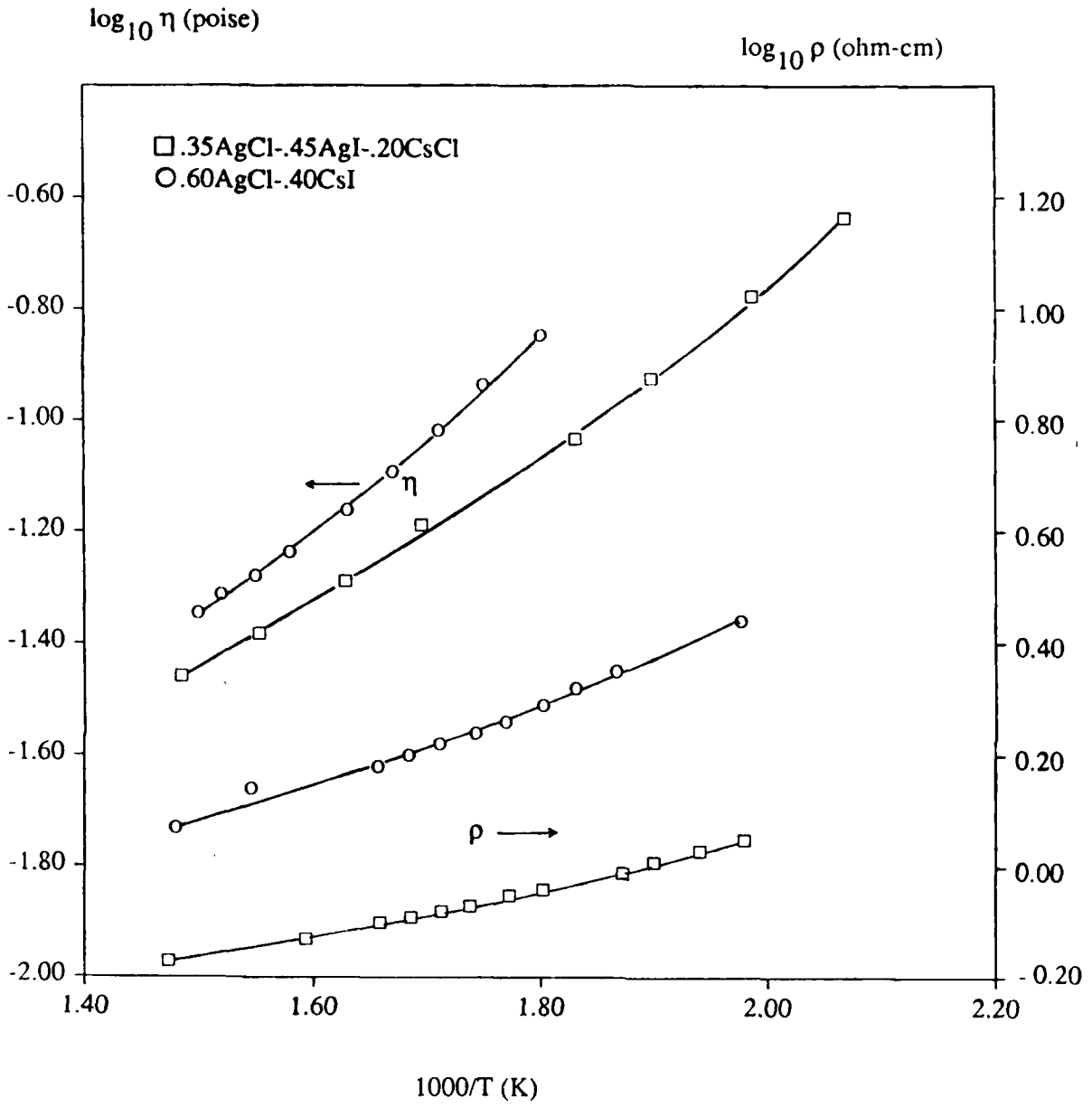
solution at two different temperatures showing definition of the DC resistivity.

Figure 3. Viscosities of the two sodium triflate solutions of Fig. 2 in Arrhenius plot form. Insert: DSC scans through the glass transition region for different molecular weight pure polymers and the two sodium triflate solutions of this study.

Figure 4. T_g-reduced Arrhenius plot of shear and conductivity relaxation times for the two melts of the study, including conductivity times measured in the glassy state.

Figure 5. Reduced temperature plot of activation energies for resistivity and viscosity of the polymer solutions of this study (notation: NaTr 16/425 ≡ sodium triflate at concentration O/Na = 16 in PPG of mol. wt. 425) compared with corresponding plots for the liquid fast ion conducting salt mixture. Figure includes data for a model molten salt system $2Ca(NO_3)_2 \cdot 3KNO_3$ which is a poor conductor in the glassy state (coupled system) and a simple tetrasubstituted ammonium iodide in which both ions are large (coupled system). Note diverging activation energies as T_g is approached in all cases except the conductivity of the fast ion salt melt. *Insert*: Reduced Arrhenius plot of viscosities of liquids of this study, excluding the PPG 4000 solution, and selected others to indicate their position within the strong-fragile pattern for glass-forming liquids[21]. T_g here is chosen as the temperature of the calorimetric glass transition from 10° min scanning.

Figure 6. Reduced Arrhenius plot of specific conductivity for the melts and solutions of this study compared with behavior of fully coupled fully dissociated $LiCl \cdot 5H_2O$ system and large ion molten salt (R_4 NI). Data from rubbery polymer PPG (106) (Ref. 15) are included for comparison.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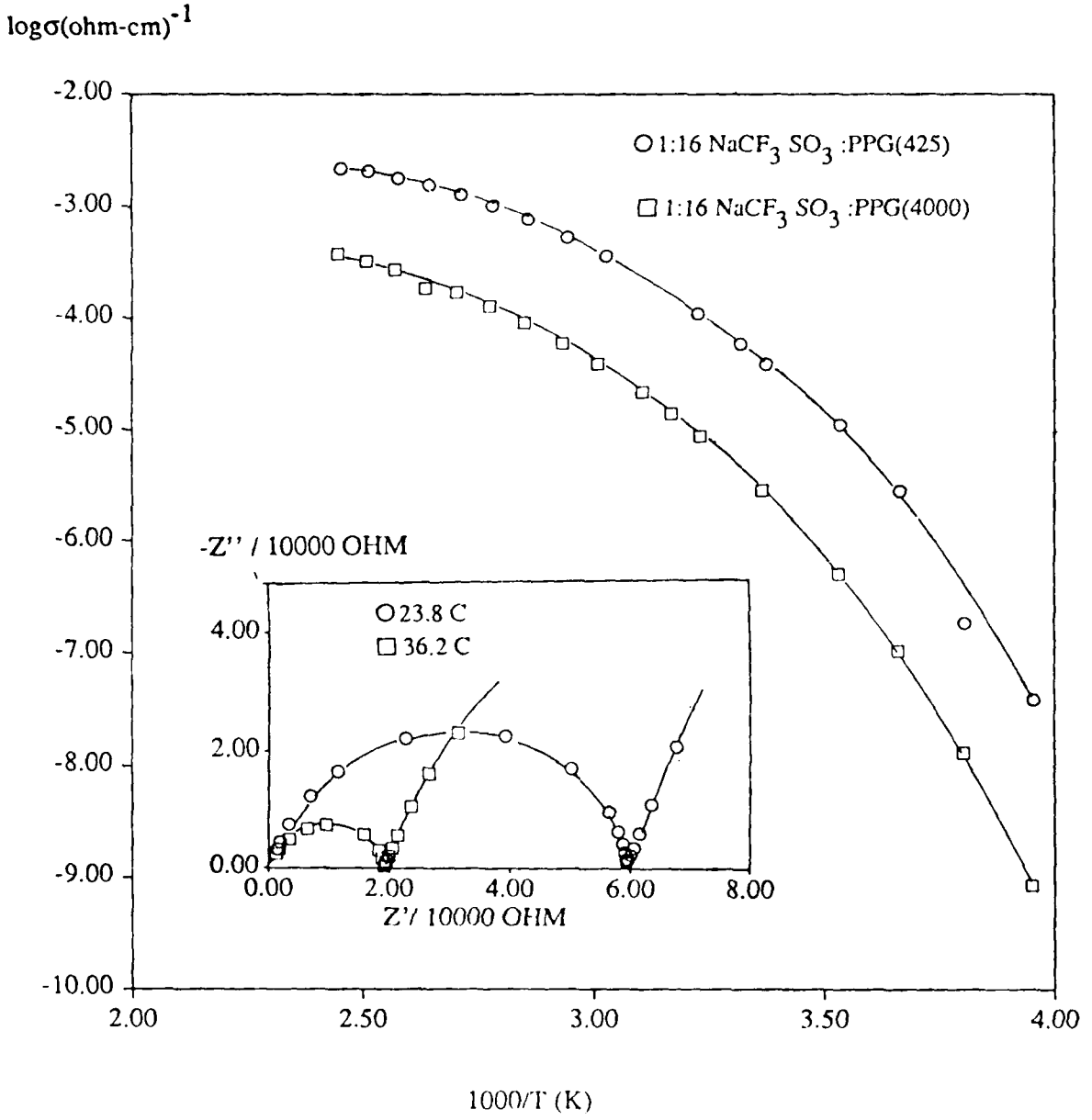
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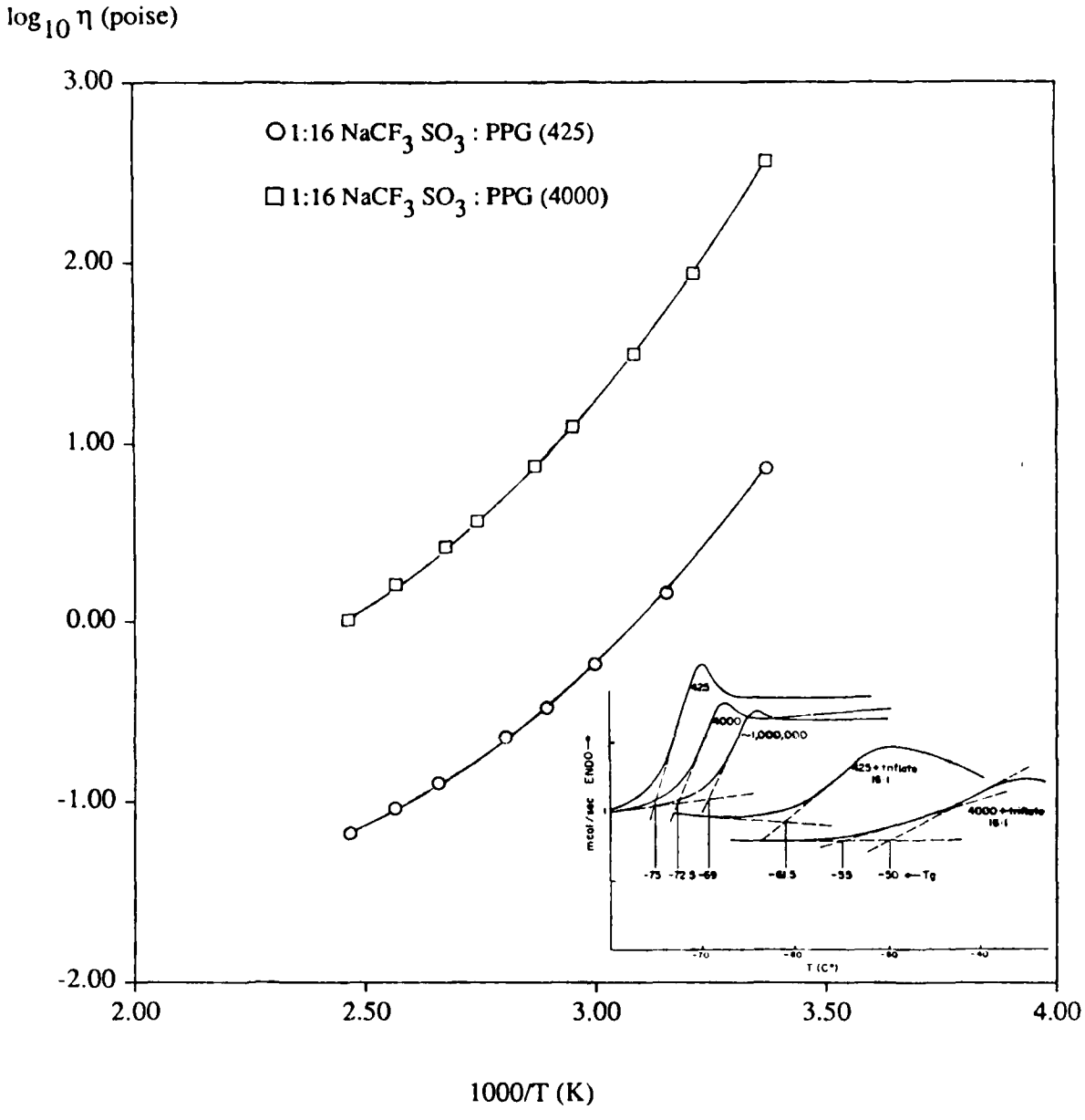
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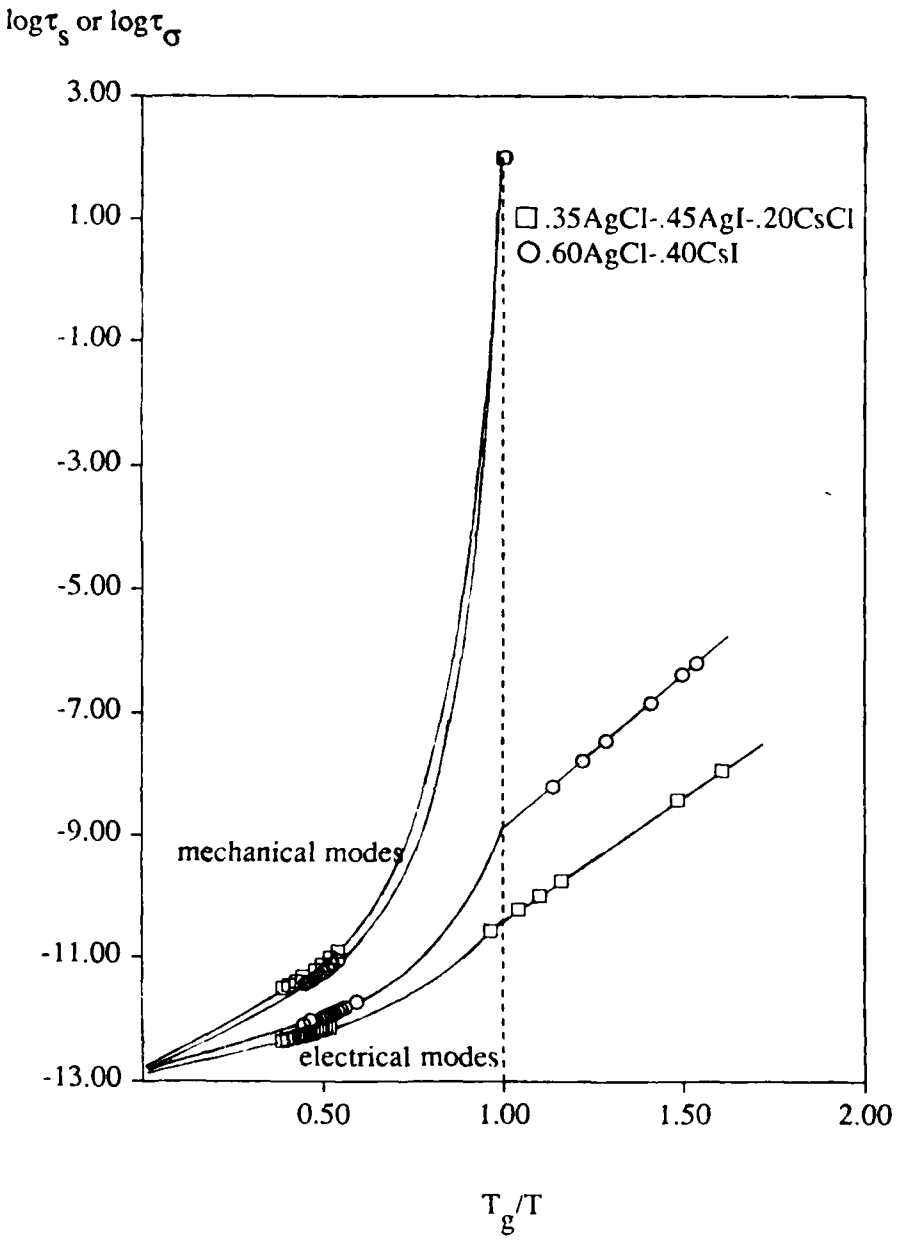
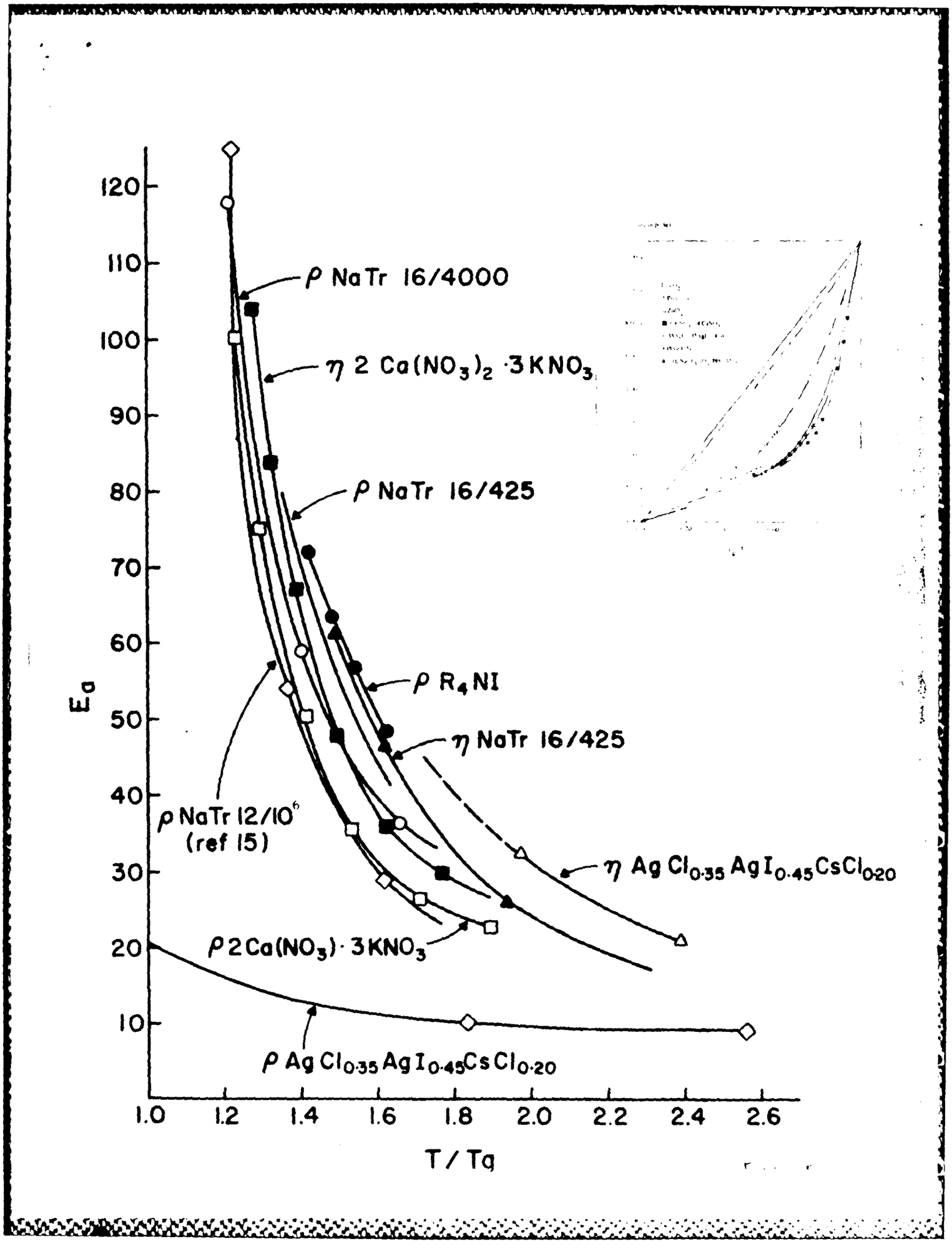
-50 ← Tg
-70
-60
-50
-40
T (C°)

Fig


logτs or logτσ
3.00
1.00
-1.00
-3.00
-5.00
-7.00
-9.00
-11.00
-13.00
□ .35AgCl-.45AgI-.20CsCl
○ .60AgCl-.40CsI
mechanical modes
electrical modes
0.50
1.00
1.50
2.00
Tg/T


120
110
100
90
80
70
60
50
40
30
20
10
Ea
ρ NaTr 16/4000
η 2 Ca(NO3)2 ·3KNO3
ρ NaTr 16/425
ρ R4NI
η NaTr 16/425
ρ NaTr 12/10^6
(ref 15)
η Ag Cl0·35 Ag I0·45 Cs Cl0·20
ρ 2Ca(NO3)·3KNO3
ρ Ag Cl0·35 Ag I0·45 Cs Cl0·20
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
T / Tg

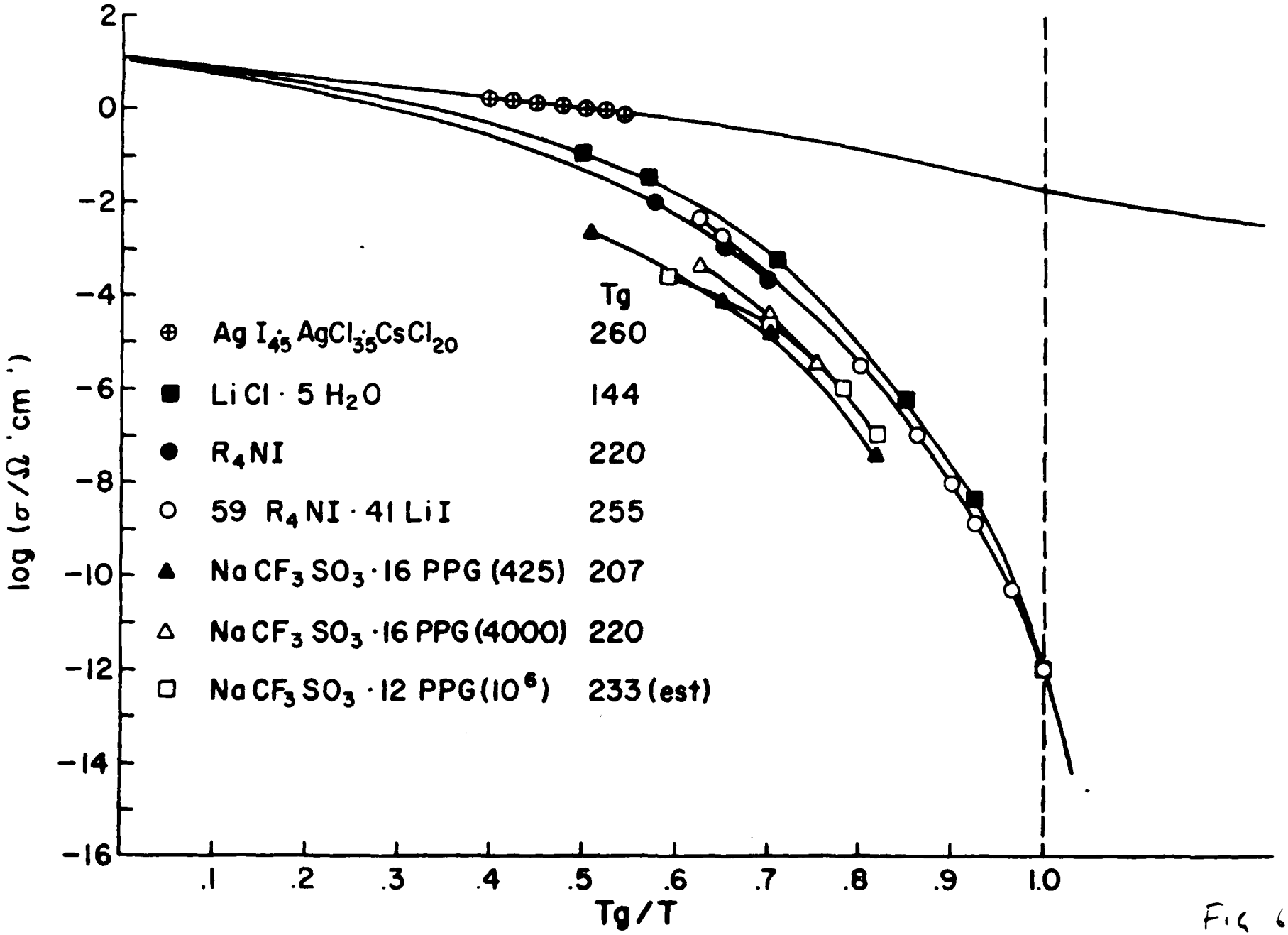

2
0
-2
-4
-6
-8
-10
-12
-14
-16
log (σ/Ω⁻¹cm⁻¹)
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
Tg/T
Tg
⊕ Ag I₄₅ AgCl₃₅CsCl₂₀ 260
■ LiCl · 5 H₂O 144
● R₄NI 220
○ 59 R₄NI · 41 LiI 255
▲ Na CF₃ SO₃ · 16 PPG (425) 207
△ Na CF₃ SO₃ · 16 PPG (4000) 220
□ Na CF₃ SO₃ · 12 PPG (10⁶) 233 (est)

Fig 6

END

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